Patterning of narrow Au nanocluster lines using V_2O_5 nanowire masks and ion-beam milling

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A shadow mask technique employing V_2O_5 nanowires and ion-beam milling is used to define narrow lines of monolayer-encapsulated Au nanoclusters. When positioned between electrodes these lines are shown to be conducting and to have nonlinear I-V characteristics with non-zero threshold voltages consistent with Coulomb blockade.

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In recent years there has been considerable interest in metallic and semiconducting nanoclusters for a variety of reasons, not least of which is their potential for electronics and sensors.[1] Although there are worthwhile applications of these clusters in devices at the micron scale, e.g., in chemical vapor sensing[2], the most intriguing possibilities arise when the numbers of clusters are reduced to a relative few and the inherent scalability associated with their nanoscale dimensions is fully exploited. One set of such possibilities involves metallic nanoclusters whose ultra-small sizes (<2-3nm in diameter) imply large charging energies and hence strong Coulomb blockade even at room temperature. For the blockade phenomenon to be manifested in an electrical signal one needs to minimize statistical averaging effects by having only small numbers of nanoclusters participate in the transport processes. The extreme example is the limit of a single cluster that has been studied extensively using scanning tunneling microscopy (STM).[3] A more practical configuration involves "small" numbers of clusters arrayed between two nanoscale electrodes defined on the surface of an insulator with possibly a third terminal situated on the surface or on the backside. This arrangement has been explored in a number of experiments and a variety of Coulomb blockade signatures have been observed. In the simplest case, the restriction on the numbers of clusters comes about merely by having small enough electrodes and relying on the Coulomb threshold to suppress fringing currents.[4] More sophisticated efforts position the clusters between the electrodes using e-beam lithography[5], atomic force microscope (AFM) manipulation[6] or electrostatic trapping[7]. Although these latter methods work, they have drawbacks including that they have not yet been successful with ultra-small clusters. In the present work, we report a simpler technique that uses nanowires to pattern the clusters (of any size) into narrow lines between electrodes.

The nanoclusters used in this study are composed of gold cores encapsulated by a monolayer shell of alkanethiol. They are prepared using a synthesis similar to that reported by Brust,[8] where the core size and shell thickness can be varied by respective control of the Au:RSH stoichiometric ratio and selection of the alkanethiol chain length.[9] The particular clusters used here had a core diameter of approximately 1.8nm and a hexanethiol shell approximately 0.4nm thick.

For the masks we use V_2O_5 nanowires that are prepared using the methods of Refs. 10 and 11. The V_2O_5 nanowire dimensions can be influenced by the growth conditions including the temperature and the possible presence of modification agents. Room temperature synthesis produces rectangular V_2O_5 nanowires that are 10nm wide and 1.5nm thick by mixing 0.1g ammonium (meta) vanadate and 1g of DOWEX 50WX8-100 in 10ml of H_2O. For this work, the growth conditions were modified so as to obtain larger nanowires by adding 0.02g N-methylformamide and heating the solution to 60C for two hours after mixing. As measured by AFM, the wires grown in this way were typically ~30nm in width, ~5nm in thickness and many microns long as a result of being allowed to grow for at least 5 days. A key advantage of the V_2O_5 nanowires is that they are readily removed (by etching in dilute HCl) after ion beam milling without damaging the clusters. This contrasts with carbon nanotubes, which we and others[12] have found harder to remove.

Our approach to defining cluster lines employs a technique much like that of Sordan *et al*[13]. In their work V_2O_5 nanowires were deposited on a AuPd film and then used as a shadow mask for Ar ion milling. Here we use an identical procedure but applied to a film of Au nanoclusters as depicted in Fig. 1. The process starts (Fig. 1, step a) with a pre-patterned substrate in which Cr/Au electrodes have been defined on a Si/SiO_2 substrate. Clusters are then self-assembled

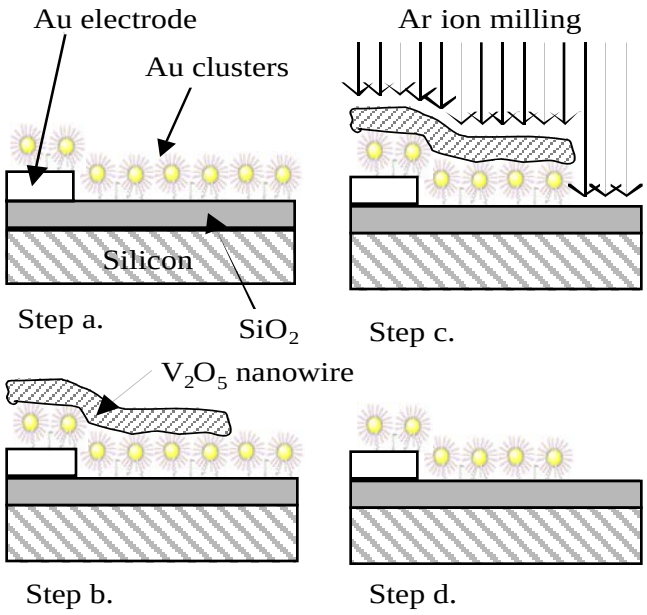

Fig. 1. Process for making nanocluster lines using V_2O_5 nanowires and ion milling.

on the substrate using an alkanedithiol linker molecule for attaching the clusters to the electrodes and (mercaptopropyl)tri-methoxysilane as a linker for attaching them to the SiO_2 substrate.[14] Next the V_2O_5 wires are deposited (Fig. 1, step b) by dipping the substrate in an aqueous V_2O_5 nanowire solution for five seconds, rinsing with water and blowing dry with nitrogen. By controlling the direction of rinsing and drying, the nanowires can be preferentially oriented so as to bridge the gap between electrodes. Ar ion milling is then used to remove the clusters that are not protected by the V_2O_5 wires (Fig. 1, step c). The milling rate for a single-layer cluster film as a function of milling time, as evaluated by XPS, is plotted in Fig. 2; we typically use 200V Ar at 2.2W/cm^2 for 15sec. An important question regarding this step (which was not an issue in Ref. 12) is whether the ion milling damages the organic shells of the clusters under the wires and possibly fuses their gold cores or otherwise affects their transport characteristics. The evidence presented in this paper indicates that this does not happen and that ion milling is therefore a useful tool for defining cluster patterns. The final step in the fabrication process is removal of the V_2O_5 nanowires (Fig. 1, step d). Their removal is desirable because they are semiconducting[15] and if left in place they can obscure and even dominate the cluster conductivity at least at room temperature as discussed below.

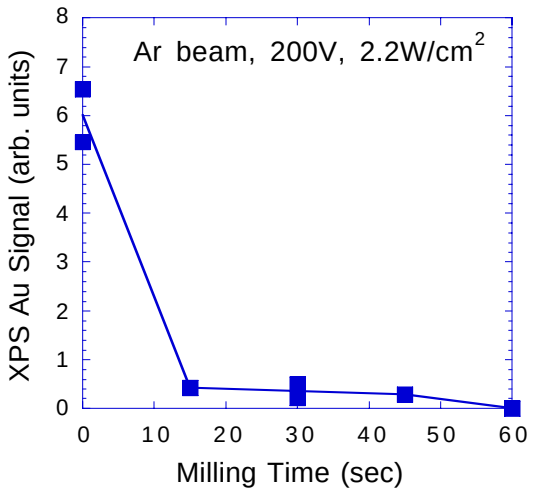

Fig. 2. Milling rate of a single Au nanocluster layer as monitored by XPS.

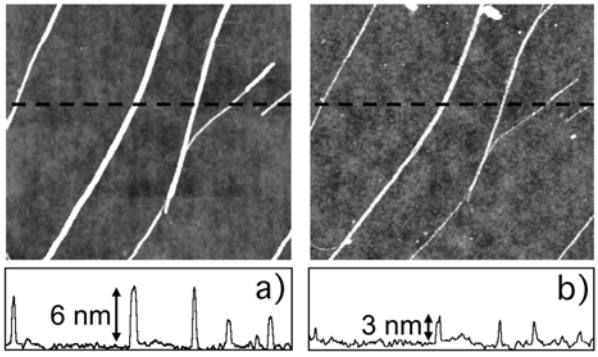

Fig. 3. AFM images and profiles of cluster lines (a) before and (b) after V_2O_5 nanowire removal.

To verify that the process of Fig. 1 can indeed create cluster lines, we characterized our samples with AFM. The images in Fig. 3 show a test sample (with no electrodes) that had clusters assembled on the substrate and then V_2O_5 nanowires deposited on top. The image in Fig. 3a is from after milling but before the V_2O_5 nanowires were removed (Fig. 1, step c), and Fig. 3b is from after their removal (Fig. 1, step d). The measured profiles (also shown in Fig. 3) confirm that the removal of the nanowires decreases the height of the lines by roughly the expected amount. The lines left behind (Fig. 3b) are about 2-3nm in height and are thus almost certainly formed of a single layer of Au nanoclusters. In a final AFM image in Fig. 4, a device with a micron-size gap is shown with the V_2O_5 shadow mask in place.

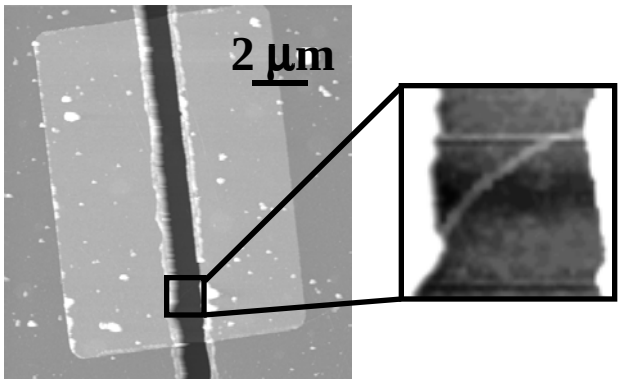

Fig. 4. AFM image of electrodes with a micron-size gap and a V_2O_5 shadow mask.

Electrical testing of the cluster lines was performed using a micro-manipulated cryoprobe system (Janis CT-420) that allows measurements to be made on unbonded devices at temperatures down to 5K. The devices tested had electrodes spaced approximately 30nm apart and were usually connected with only a single line of clusters defined by the V_2O_5 wires. The current-voltage (I-V) characteristics typically seen in

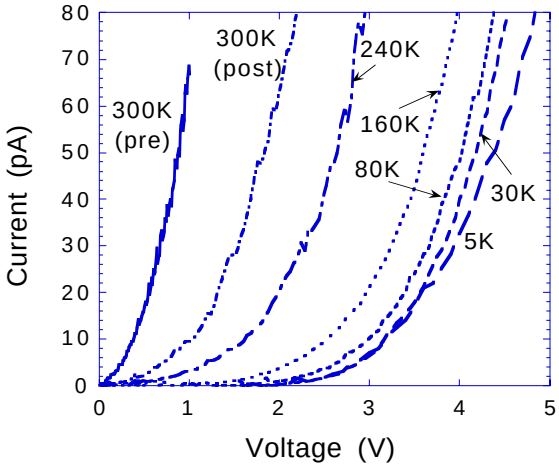

Fig. 5. I-V characteristics with temperature as a parameter for a V_2O_5-defined cluster line between two electrodes spaced ~30nm apart.

these devices are plotted in Fig. 5 as a function of temperature. The curves are strongly nonlinear and show a non-zero threshold voltage. For the particular device studied in Fig. 5 the V_2O_5 nanowire was still in place. That this wire conducts some current, at least initially, is shown by the difference in the I-V characteristics at 300K before (pre) and after (post) thermal cycling down to 5K. Apparently, differential thermal expansion moves, damages or dislodges the nanowire, thereby raising the contact resistance and causing the current through the cluster film to become dominant. In addition, as the temperature is lowered below 300K any residual nanowire current would decline exponentially (as a result of the Schottky barrier contact between the electrode and nanowire) and would quickly become completely negligible.[15] The minimal contribution of the V_2O_5 nanowire to the conduction observed in Fig. 5 was further demonstrated by removing the nanowires by etching in dilute (5%) HCl. Unfortunately, a direct comparison with such data is problematic because residual ions that possibly remain behind after the etching can bias the clusters and cause significant threshold shifts. Nevertheless, the shapes of the I-V curves (not shown) remain the same, again confirming that the cluster conduction is dominant.

The clearest evidence that the currents seen in Fig. 5, especially at temperatures below 300K, is obtained from a closer examination of the I-V curves themselves. These curves do not display temperature-activated characteristics (associated with current flow over a Schottky barrier) but rather show a power law dependence --- $I \sim (V - V_T)^{\zeta}$ with an exponent (ζ) greater than one and a non-zero threshold voltage (V_T) --- that is commonly

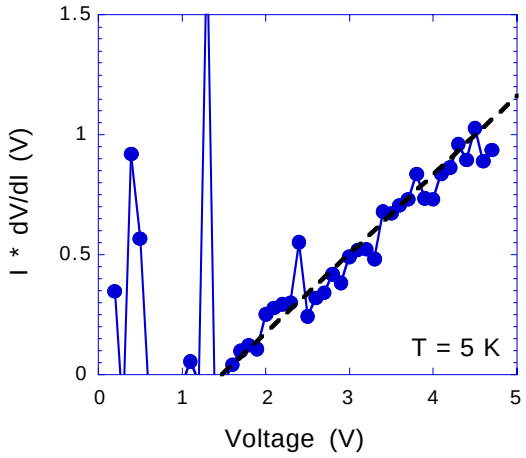

Fig. 6. The data in Fig. 5 for 5K plotted as dV/dlnI versus V. The linearity shows that power law behavior is observed and allows an accurate determination of V_T.

associated with cluster transport[4]. This is best shown by the fact that, when the data is plotted as dV/d(lnI) versus V in Fig. 6 (for the 5K data), a straight line is obtained. From the slope and intercept of this line we infer that $\zeta \sim 3$ and $V_T \sim 1.5V$ (for this sample at 5K). Plotting the data at other temperatures in the same way we find that ζ is fairly constant, but that the threshold voltage varies linearly with temperature as shown in Fig. 7. This too --- including the fact that V_T is found to go negative --- is remarkably similar to the behaviors reported previously for single-layer cluster transport between nanoscale electrode fingers with a gap and width of similar dimensions.[4] This is strong evidence that "normal" cluster transport is occurring and that the V_2O_5 process therefore represents a viable technique for creating narrow cluster lines.

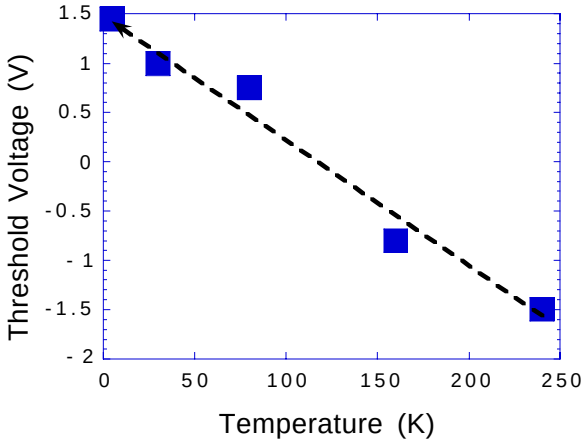

Fig. 7. V_T values determined from plots like Fig. 6 as a function of temperature. The linearity observed is characteristic of cluster transport.

To summarize, in this work we have demonstrated that narrow Au nanocluster lines can be fabricated using a process in which V_2O_5 nanowires are employed as a mask for ion-beam milling. These single-layer cluster lines are conducting and show non-zero threshold voltages and nonlinear I-V characteristics likely associated with Coulomb blockade. This electrical behavior is quite similar to that previously observed in unpatterned clusters assembled between nanofinger electrodes.[4]

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